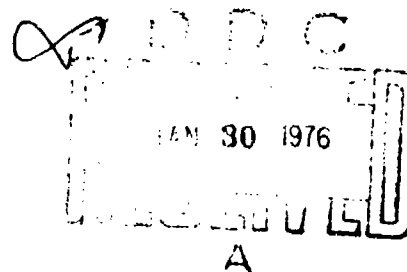# NSWC
TECHNICAL REPORT

WHITE OAK LABORATORY

SPONTANEOUSLY COMBUSTIBLE SOLIDS--A LITERATURE STUDY

By
Eleonore G. Kayser
Carl Boyars

May 1975

NAVAL SURFACE WEAPONS CENTER
WHITE OAK LABORATORY
WHITE OAK, SILVER SPRING, MARYLAND 20910

●APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

JAN 30 1976

A

NAVAL SURFACE WEAPONS CENTER
WHITE OAK, SILVER SPRING, MARYLAND 20910

NOTICE

The contents of this report reflect the view of the Naval

Surface Weapons Center, which is responsible for the facts

and the accuracy of the data presented herein.   The contents

do not necessarily reflect the official views or policy of

the Department of Transportation.   This report does not

constitute a standard, specification or regulation.

This document is disseminated under the sponsorship of the
Department of Transportation in the interest of information
exchange.   The United States Government assumes no liability
for its contents or use thereof.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC/WOL/TR-75-159	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SPONTANEOUSLY COMBUSTIBLE SOLIDS -- A LITERATURE SEARCH		5. TYPE OF REPORT & PERIOD COVERED Final Report. April - October 1974 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Eleonore G. Kayser Carl Boyars		8. CONTRACT OR GRANT NUMBER(s) DOT-AS-40049
9. PERFORMING ORGANIZATION NAME AND ADDRESS Explosives Division Naval Surface Weapons Center White Oak, Silver Spring, Maryland 20910		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NSWC-1028/DOT
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE May 1975 13. NUMBER OF PAGES 34
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

This research was monitored by the Department of Transportation, Office of Assistant Secretary for Environment Safety and Consumer Affairs, Office of Hazardous Materials, Washington, D. C.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Pyrophoric Materials
Spontaneously Combustible Solids
Air-Hazardous Materials
Water-Hazardous Materials
Hazardous Materials
Transportation Hazard

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Existing information on spontaneously combustible solids including pyrophoric-air hazardous materials and water reactive materials has been reviewed. Pertinent data on (a) the causes and prevention of spontaneous combustion in organic and inorganic materials due to air and water reactivity, (b) the application of various mathematical treatments to spontaneously combustible materials, and (c) available test methods for assessing the flammable properties of spontaneously combustible materials, e.g., autoignition temperature and spontaneous heating are also included.

DD FORM 1473 1 JAN 73   EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

NSWC/WOL/TR 75-159   May 1975

Under Interagency Agreement DOT-AS-40049, the Naval Surface Weapons
Center, White Oak Laboratory, has completed a literature survey
of all attainable data pertaining to spontaneously combustible
solids including pyrophoric-air hazardous and water reactive
materials. All available hazard classification systems and test
methods relating to spontaneous combustion have been reviewed and
evaluated. Pertinent data on (a) the causes and prevention of
spontaneous combustion in organic and inorganic materials due to
air and water reactivity, (b) the application of various mathemati-
cal treatments to spontaneous combustion, and (c) available test
methods for assessing the flammable properties of spontaneously
combustible materials e.g., autoignition temperature and spontaneous
heating are also included. This is the final report under that
agreement. Use of trade names herein does not constitute any
endorsement of the products named.

                                        Julius W. Enig
                                        JULIUS W. ENIG
                                        By direction

1

TABLE OF CONTENTS

LIST OF TABLES

INTRODUCTION

The Department of Transportation's Hazardous Materials Regulations Board is considering the adoption of regulations that would provide a more complete identification of the stability characteristics and therefore the potential hazards associated in the transport of hazardous materials. A number of materials are designated as flammable solids on DOT's commodity list because of a history of spontaneous ignition occurring either in transit, in handling, or in storage.

Currently DOT/OHM has inadequate technical data to define quantitative criteria for the hazard classification of these materials. Therefore, there is need for a theoretical evaluation of materials which could be designated "spontaneously combustible." The purpose of this investigation is to provide technical background for use in developing regulations for the transportation of such materials. At present, there is neither international agreement on regulations concerning the shipment of flammable solids nor a standard classification test method for flammable solids in the transportation regulations.

In DOT terminology, "flammable" characterizes a greater degree of fire hazard than "combustible" (excluding spontaneously combustible). Spontaneously combustible materials differ from readily flammable materials in that the latter will ignite within a specified time limit (a few minutes) and burn rapidly when exposed to a specific ignition source. Ignition sources include hot surfaces, hot filaments, flames, hot gases, electric sparks, and adiabatic compression of the material itself. Spontaneously combustible materials can inflame even in the absence of what are normally regarded as ignition sources. Although one can regard such materials as a sub-class of flammable solids and liquids (current regulations), many spontaneously combustible substances may not ignite within the specified time limit in a test designed to characterize flammable materials. This is especially true when the heat-generating reaction in the spontaneously combustible material is one involving bacterial action. Also, the test for flammable materials may be performed on a sample size which is less than the critical mass necessary for spontaneous combustion to occur in some substances.

Further sub-classification of spontaneously combustible materials includes pyrophoric materials, i.e., those that will ignite spontaneously on exposure to air (air-hazardous material) and those that will ignite on contact with water or moisture (water-hazardous materials).

Causes of Spontaneous Combustion in Some Organic Materials (Ref: 1-13)

Organic materials which are subject to spontaneous ignition at ordinary ambient temperatures must have access to atmospheric oxygen or carry oxidizer in some reactive form and be raised to a kindling or autoignition temperature by the exothermic reaction. Moisture is, in some cases of spontaneous combustion, essential for the resulting reaction. Bulk transport and/or storage may result in spontaneous ignition in many agricultural products.

3

Low temperature oxidations of substances such as beet sugar and coal can be directly related to their adsorption capacities for atmospheric oxygen, with desorption of the oxidized products. Adsorption in general is accompanied by the liberation of energy in the form of heat. The temperature increase depends on the rate of heat transfer to the surroundings. Higher temperature accelerates the chemical reactions with adsorbed oxygen, which in turn provide an even greater heat release. Thus, physical adsorption is followed by subsequent chemical oxidation and spontaneous ignition if the heat is not dissipated to the surroundings sufficiently rapidly to prevent achieving the autoignition temperature in the material.

The oxidizing action of microorganisms in organic materials such as hay and sawdust often produces the initial heat which eventually leads to spontaneous combustion. In this process, the product is changed chemically and physically by bacteriological action. Fermentation and action by microorganisms can raise the temperature to about 130°F. Chemical oxidation of fermentation products then occurs. When the temperature reaches 212°F, the microorganisms are destroyed. Chemical action involving the cellulose can further increase the temperature. If the heat cannot be dissipated to the surroundings, the temperature within the material continues to rise and the rate of oxidation increases. Eventually the material reaches its autoignition temperature, where combustion occurs. In general, the conditions essential for spontaneous combustion where bacteriological action is involved are an existing slow oxidation and good heat insulation.

Spontaneous Ignition--Mathematical Treatments (Ref: 14-24)

Ignition produced by the generation of heat within a material which is decomposing can be treated by thermal explosion theory. Frank-Kamenetskii's treatment is approximately valid for any exothermic decomposition in which heat evolution obeys an Arrhenius law with a constant energy of activation to represent the dependence of zero order reaction rate upon temperature. This Arrhenius relationship of course does not hold for microbiological processes (and is questionable for many complex chemical processes). Walker attacks the approximation involved in application of the binomial theorem to the Arrhenius law by Frank-Kamenetskii. Walker's treatment relates critical size to critical ambient temperature for self-heated materials undergoing reactions of zero order even when the effects of temperature on reaction rate are non-Arrhenius. Van Geel, starting with the Frank-Kamenetskii treatment, introduces the concept of a safe radius, that is, a critical dimension for which the temperature difference between the center of a self-heating material and its surroundings does not increase more than 10°C during the storage period. He shows this to be useful over a considerable range of activation energy values.

All applications of mathematical treatments of spontaneous ignition require a knowledge of the apparent activation energy of the overall heat evolution reaction or some other means of specifying

dependence of reaction rate on temperature. All involve an approximation of zero order reaction kinetics. This is valid in general only for reactions in which nearly all the originally reacting substance is still present or else as an approximation for a specific instantaneous state. Prediction of the likelihood of occurrence of spontaneous combustion depends, in addition, on knowing the specific heat of the material, its bulk density, thermal conductivity coefficient, heat transfer coefficient to the surroundings, and temperature of the surroundings as well as the heat evolution rate per unit mass; it also depends, of course, on the amount and geometric shape of the material undergoing self-heating.

Flammability Determinations (Ref: 25-35)

Spontaneous Ignition Temperature (Ref: 25-30)

The thermal properties of spontaneously combustible materials which are normally determined by the chemical industry include auto-ignition temperature and spontaneous heating. The autoignition or spontaneous ignition temperature is defined as the lowest temperature at which a substance in either gas, liquid, or solid state, in the presence of air will ignite after a certain delay without the application of any artificial means of ignition. Factors influencing autoignition temperatures include the size and shape as well as the physical and chemical properties of the material being tested. Methods which have been employed for the determination of spontaneous ignition temperatures include (a) crucible methods--static (Moore Apparatus, Krupp Ignition Meter, Jentzoch Ignition Meter and ASTM D 2155-66) and dynamic (The Royal Aircraft Establishment (Farnborough) Spontaneous Ignition Temperature Apparatus), (b) dynamic tube methods, (c) bomb methods, and (d) methods of adiabatic compression. Of the preceding methods, the crucible methods are by far the most popular (25).

The ASTM D 2155-66 may be used for the determination of the autoignition temperature of liquid or semiliquid petroleum products in air at one atmosphere pressure using a sample ejected from a hypodermic syringe. In this method, a heated 200 ml Erlenmeyer flask of borosilicate glass containing air at one atmosphere pressure is used as the test chamber. This test is carried out in a darkened room. A small sample of the test liquid is introduced into the flask. The contents of the flask are inspected during the five minutes following the sample injection. If autoignition occurs, a flame appears in the flask. Observations are carried out at a series of test temperatures and with several sample sizes. The autoignition temperature is taken as the lowest temperature at which ignition is observed (26).

Spontaneous Heating (Ref: 31-34)

The Mackey apparatus is considered a suitable general method for assessing the spontaneous heating and ignition hazards associated with the transport, storage and use of materials that are subject to

atmospheric oxidation at ordinary temperatures (31-33). This apparatus and subsequent modifications are used to detect materials' susceptibility to spontaneous heating. In general, this device consists of a water-jacketed cylinder, 4 inches in diameter and 7 inches high, the top of which is closed by a cover. The cover is pierced by a central hole and by two draft tubes each 6 inches long and 1/2 inch in outer diameter. One of these tubes extends into the cylinder and the other extends upward from the cover. A 30 g sample is placed on cheesecloth, which in turn is placed in a metal gauze cylinder (2 1/2 inches in diameter and 6 inches long, no. 12 mesh). The gauze cylinder is centered in the jacketed cylinder. Water in the jacket is brought to a boil, the sample on the cheescloth in the gauze cylinder is introduced, and a thermometer is placed in the central hole (31). If the sample temperature does not exceed 100°C within an hour, the material is judged safe with regard to tendency for spontaneous heating. A thermocouple with recorder would provide a safer and more accurate test. The test is useless for substances which ignite as a result of slow oxidation and for materials where biological processes can cause spontaneous ignition.

There is currently, no standard method available for assessing extremely flammable solids (pyrophoric powders) which can ignite spontaneously on exposure to air at ambient temperature. A test developed by the Bureau of Explosives (American Association of Railroads) for pyrophoric liquids is considered by a United Nations working group to be adaptable to some solids but not to powderlike materials. This method requires rather large quantities of material and involves the use of a sawdust reacting medium, although the particle size, moisture content, and type of sawdust are not specified. A maximum relative humidity of 75% is also specified, which according to the Bureau of Mines, may not be high enough to evaluate the pyrophoricity of some substances (34).

The Bureau of Mines has recently developed a method for evaluating the ease of spontaneous ignition of extremely flammable solids by determining their ease of ignition using an environmental chamber at high-humidity conditions. This method utilizes small samples at ambient temperature of 90° or 130°F and at various humidity conditions. The procedure calls for an environmental chamber in which the relative himidity can be varied from 50-90% and controlled to within ± 5%. The sample is placed in the center of a 4 in. diameter by 6 in. long glass reaction tube that is mounted vertically in the environmental chamber to minimize heat losses. The reaction tube is open at both ends to permit circulation of air. The extent of the reaction is determined by visual observations nd by measuring the temperature rise near the top of the sample bed using 30-gage iron-constantan thermocouple. The output of the thermocouple is then fed to a continuous pen recorder (34). Further developments of the basic test procedure as well as a hazard classification of flammable solids for transportation can b found in reports prepared for DOT by P. V. King and A. H. Lasseigne, DOT Report TSA-20-72-6, 1972 (NTIS:PB-220084) and R. Hough, A. Lasseigne and J. Pankow, DOT Report TES-20-73-1, 1973(NTIS:PB-227019/AS).

An additional work on the hazard of flammable solids which furnishes
supplemental information on important variables occurring in several
of the tests proposed by previous investigators can be found in a
report recently prepared for DOT by C. B. Dale, DOT Report TES-20-75-2,197⁵
(NTIS: PB 240 878/AS).

For absolute assurance that a material does not represent a
spontaneous ignition hazard in transport, an adiabatic storage test
should be carried out at the maximum ambient temperature the material
is likely to encounter and for the maximum period of time that it
will be in transit (plus any additional prior storage time). Failure
to achieve autoignition under these conditions, which are equivalent
to a mass so large that there is no heat loss from the center by
thermal conduction, is conclusive evidence. One applicable apparatus
is described in a report prepared for OECD by J. W. Hartgerink (Thermal
Analysis of Unstable Substances: The Exothermal Decomposition Meter,
Ass. nr. 8357/9569, RVO-TNO, Rijswijk, The Netherlands, May 18, 1973).
It may not be necessary to carry out full-term adiabatic storage
tests on materials whose self-heating could be established by smaller-
scale screening tests such as Differential Thermal Analysis or
Differential Scanning Calorimetry, and the Exothermal Decomposition
Meter of RVO-TNO.

Water Reactivity (Ref: 35)

Moisture-or water-hazardous materials react violently with
water, generating sufficient heat to ignite combustible container
materials or the flammable gases generated by the reaction. Although
this hazard is recognized by various organizations, currently, there
is no generally accepted method to evaluate the water reactivity of
materials. A procedure for determining water reactivity by either
adding a given weight of water to a given weight of material or vice
versa has been proposed by Mason and Cooper of the Bureau of Mines (35).
In either case, the rate of the temperature increase as well as the
total temperature increase are recorded, and the gases evolved are
sampled for analysis. The test apparatus consists of a sample
container (a pyrex tube 1 3/8 in. dia. and 10 in. long) imbedded to
a depth of 3 1/2 in. in a block of insulating foam (polyurethane
or polystyrene) 3 in. square by 5 in. high. A thin piece of copper
3/8 in. square and weighing 0.5 gm is silver soldered to the tip of
a chromelalumel thermocouple which measures the temperature rise.
The thermocouple is placed in the pyrex tube so that the copper
square is covered by the sample. The output of the thermocouple
is then fed to a recorder. See also DOT reports cited in Ref. 34 discussion

Using appropriate safety precautions, an initial estimate of
the severity of the reaction is made by adding 5 gms. of water slowly
to 0.5 gm of material. The temperature rise is measured by adding
10 gms of water slowly (10-20 sec) to 1,2,5,10 and 20 gms. suc-
cessively of the sample. Measurements are continued until the
temperature peaks and then begins to drop. If 1,2, and 5 gms of
the material give virtually no temperature increase in 4 minutes,
10 gms of water are added to 10 gms of sample and the temperature

is monitored for one hour to determine if a slow reaction occurs. If the reaction is not too violent, 10 gms of water are added to 20 gms of the material to see if a temperature rise results. This procedure may also be reversed by adding the material to the water in the container (35).

If gas is evolved, a sample from the reacting material is collected through a flexible needle inserted into the reaction container to within approximately an inch of the reacting mixture. This sample is then analyzed on a chromatograph for flammable and/or toxic gases (35).

Materials Subject to Spontaneous Heating (Ref: 1-12,36-97)

Organic materials subject to spontaneous heating which can be caused by bacteriological action include hay, straw, clover, malt, grains, tobacco, seeds, fodder, fish-meal, fertilizers, garbage, sugar, etc., (1-12, 36-39, 43). The phenomena of spontaneous ignition in these materials exhibit considerable variation according to their specific natures and also the external influences to which they are subjected such as moisture content, size, exposure methods of shipping and storage. The real danger of spontaneous ignition usually occurs when the damp product is piled in large masses for storage. Experiments performed by Rothbaum, have shown that spontaneous ignition is most likely to occur in moist, permeable biological materials at relative humidities in the 95-97% range. An exception to this would be where the oxidation of unsaturated oils is involved. At relative humidity values below 95% no appreciable bacterial action takes place. Fungi are known to grow actively at relative humidities greater than 75%, although most bacteria metabolise strongly only at relative humidities over 95%.

As 100% relative humidity is approached, a rapid rise in thermal conductivity due to water vapor transfer is noted. This is responsible for large heat losses, and therefore subsequent chemical reactions will be less likely to exceed the microbiological maximum temperature limit of 76°C. The thermal conductivity of wet porous materials between 60°C-100°C has been found to be almost entirely controlled by the rate of water vapor transfer. At relative humidity values nearing 100% the thermal conductivity of moist porous materials shows a very rapid rise with temperature. Therefore, a chemical reaction of low heat output will produce a temperature increase more easily when the relative humidity is appreciably below 100%. Thus it seems likely that the biological temperature limit would be passed only by materials in equilibrium with relative humidity readings within a fairly narrow range of about 95-97% (1).

Rothbaum has found that in the spontaneous heating of hay, which is in equilibrium with a relative humidity at 95-97%, microbial action is responsbile for temperature increases to about 70°C. Chemical reactions (dependent on the presence of moisture) then increase the temperature to 170°C while further chemical oxidation

of the dry hay then leads to combustion (1). Although hay will
self-heat due to microbial action, it has been proven that chemical
heating of hay is not necessarily dependent on previous biological
activity. Rothbaum has shown that even without previous microbial
action, chemical heating can continue in hay for lengthy periods
and, under adiabatic conditions, will raise hay to its ignition
point. While the self-heating of hay has long been a subject of
concern, spontaneous ignition has never occurred in hay containing
less than 33% moisture (moisture expressed as % of dry weight).
Therefore, moisture control of this material should eliminate the
hazard of ignition.

The spontaneous combustion of sugar and bagasse (the crushed
juiceless remains of sugar cane as it comes from the mill)(40-43)
has also been reported. The self-heating of these materials which
occurred in storage bins and silos was found to be due to oxidation
influenced by fermentation. Both Actinomyces and Semiclostr dium
bacterial strains (bacteria which have been identified with
fermentations which evolve heat) were found in the decompc ed sugar
and also in the sugar from the edges of the affected areas.

Specific biochemical processes have a decisive significance
in the phenomena of spontaneous heating of many materials. One of
these processes is the utilization of proteins and the products of
their hydrolysis as a source of energy by microorganisms. The
chief energy loss in the decomposition of proteins, as reported by
Goldin, is connected not with hydrolysis but rather with the
decomposition of amino acids. The production of heat at the expense
of proteins and the products of their hydrolysis is much greater
under aerobic than under anaerobic conditions. It is practically
impossible for the decomposition of proteins under anaerobic
conditions to result in spontaneous heating since the production of
heat is related to oxidation processes. Certain organic acids,
such as acetic, propionic, and ascorbic, are strongly inhibitory
to mold and bacterial growth. The calcium and sodium salts of
propionic acid are normally used in fruits and vegetables to inhibit
the growth of molds. Propionic acid has also been used to prevent
microbial deterioration in grain (moist wheat and cornmeal) for at
least twelve months if the pile is protected from the rain. In
addition to being antimicrobial, propionic acid and its salts stop
respiration of the living cells in stored grain, thereby inhibiting
any heat buildup in the pile.

Mixtures of nitrates with easily oxidized materials (fertilizer
mixtures) are also a recognized fire hazard due to their ability to
self-heat. Excessive development of heat in curing piles of
fertilizers (44,45) containing superphosphate, organic matter, and
large amounts of inorganic material can be traced to the oxidation
of organic matter by nitric acid, which is formed in the reaction
between the nitrate and free phosphoric acid. The rate of the
reaction as reported by Davis and Hardesty, is accelerated by
increases in (a) concentration of free phosphoric acid in the
liquid phase of the fertilizer, (b) size and insulating properties

of the curing pile, (c) amount and mobility of the liquid phase in the mixture, and (d) degree of interaction among the active ingredients of the mixture. The degree to which these conditions are fulfilled will determine the extent of the temperature rise. Under certain conditions the heat generated by the oxidation reaction is sufficient to cause spontaneous ignition in a base mixture stored at 30°C. The reaction leading to ignition of such mixtures containing super-phosphate, ammonium nitrate, and organic conditioner can be prevented by treatment of the superphophate with ammonia (45).

Animal and vegetable fibers (3,10,11,46) such as wool, silk, cotton, jute, hemp, flax, shoddy, etc., are also susceptible to autooxidation which can lead to spontaneous ignition. Animal fibrous materials are in general less susceptible to spontaneous ignition than vegetable fibers, since hollow fibers (vegetable fibers) constitute a greater danger in their behavior toward fire than do solid fibers because of their tendency to absorb oxidizing foreign materials. Animal fibers, in general, when ignited will not support combustion while vegetable fibers will smolder and burn. Both animal and vegetable fibers which have been in contact with animal or vegetable oils are subject to self-heating and spontaneous combustion.

Cotton waste (4,7,10,11) when in contact with fatty oils is more susceptible to autoignition then animal fiber. The autoignition is dependent on the properties of the oils with which the fibers are in contact. The more unsaturated oils are the most hazardous because of their ease of oxidation. The presence of moisture is also an aggravating factor responsible for autoignition. Mineral oils while less subject to oxidation because of their negligible affinity for oxygen, cannot be absolved from the autoignition hazard, although they are sometimes used as a means of reducing the danger of spontaneous ignition by mixing with other more hazardous oils.

Although heat is developed by friction at baling, by bacterial activity in wet wool, and by moisture adsorption on over-dried wool, direct oxidation of wool (47-53) seems to be the main process leading to temperatures high enough to cause ignition. Sheared and slipe wools (wools that contain little or no fat or oil) do not ignite. Experiments by Walker, Williamson and Carrie et al., using ether-extracted fat from pie wools (wools removed from sheepskin by the pie process contaminated with subcutaneous fat) demonstrated that the self-heating reaction is associated with the fat and not the wool. The heating reaction in wool is caused by the atmospheric oxidation of unsaturated components of fat. It has been suggested that traces of water vapor are necessary to catalyse this oxidation, however no such effect could be detected in experiments on dried wool by Walker and Williamson. However, the influence of water is revelant to the problem. Bales of wet or damp wool can become hot due to microbiological action. Microbiological heating of wet wool must therefore be considered as a possible trigger mechanism to preheat bales of wool to a point where oxidation could commence, since previous experiments have shown that the oxidation of pie fat (fat extracted from pie wools) can take place in the presence of considerable moisture.

Soybeans and soybean by-products (3,10,39,55-57) are an example
of another common agricultural product in which spontaneous combustion
can occur. The oxidation and thermal polymerization of the unsaturated
oils present in soybeans (approximately 10 times as much unsaturated
oil as wheat) is considered responsible for the ease with which
chemical heating takes place. Although a high moisture content is
considered a primary cause of spontaneous ignition in some agricultural
products (hay, grains, fodder, etc.) the principle cause of spontaneous
ignition in soybeans and soybean by-products appears to be the
oxidation and polymerization of the unsaturated oils, with moisture
considered a contributing factor. As in the case of other common
oxidizable vegetable oils, the actual spontaneous ignition hazard
presented by soybeans will depend upon the circumstances including
(a) the amount of oil involved, (b) the ambient temperature (c) the
conditions with respect to heat transfer and dissipation and (d) the
presence of other combustible materials.

Clay-diluted chlorinated insecticides (54) occasionally decompose,
sometimes becoming sufficiently hot to ignite spontaneously. The
decomposition of insecticides occurs in wettable powders and dusts
as a result of the catalytic action of the clay diluent. Investiga-
tions have shown that this decomposition is promoted by the acid
sites of the clay. The rates of reaction of these insecticides
in the presence of various clay diluents were found to increase
with the increasing acidity of the clay surface. Treatment of the
clays with volatile organic bases or basic substances such as urea
or hexamethylenetetramine, has been found to reduce the acid strength
and diminish the rate of decomposition accordingly. Since the
introduction and use of these clay-deactivators, the problem of
decomposition has virtually disappeared.

Animal and vegetable oils (10,25,58-60) in the presence of air
and at ambient temperatures, undergo oxidation with the evolution
of heat. Although their ignition temperatures are comparatively high,
the heat generated by oxidation is sufficient in some cases to cause
ignition under favorable circumstances. This susceptibility to
spontaneous ignition is greatly increased by exposing a relatively
large surface area of the oil to the oxygen in the air (e.g.,
impregnating a waste material such as sawdust, cotton, rags, etc.).
The form in which the oily fibrous material is exposed to the air
also influences the reaction and affects the rate of dissipation of
heat. If the oily mass is compact, the oxygen supply from the
atmosphere is necessarily restricted, and if exposed to air currents,
the heat loss may prevent a rise in temperature. However, a reaction
can begin (given enough oxygen) that can generate considerable heat
which is accumulative due to the insulating power of the waste and
this heat can then accelerate further reaction and finally result
in ignition.

Available evidence indicates that wood when subjected to
continuous heating will form a pyrophoric type carbon which is
liable to ignite spontaneously at low temperatures. Sawdust and
wood chips (10,11,61-75) also have a tendency to spontaneously

ignite when stored in large piles. This tendency is increased when
the materials are impregnated with vegetable or animal oils, glue,
organic dyes, etc. Nitric acid which fosters internal heating and
combustion can also cause spontaneous combustion in sawdust. The
initial heat release in a chip pile is the result of oxidative
processes occurring within or on the surface of the wood chips.
This heating is the direct result of (a) respiration of the living
cells, (b) bacterial growth-microorganisms on or within the wood
indirectly oxidizing the various wood constituents, (c) direct
chemical oxidation - readily oxidizible materials such as unsaturated
fatty acids and other extractives entering into combination with
atmospheric oxygen by direct chemical reactions, and (d) fungal
growth. The initial heating observed in the first few days of chip
storage is apparently caused predominately by (a), (b), and (c).
The direct chemical oxidizations probably become important above
42°C. The contribution of fungal growth to the heating observed in
wood chips is most likely significant only after everal weeks of
outside storage. Several factors which influence these oxidative
processes include (1) chip pile temperature, (2) species of wood,
(3) moisture content, (4) climatic conditions, (5) pile size and
height, and (6) the amount of foreign material. Losses in wood
substance from the action of microorganisms in wood chips stored
outside average roughly about 1%/month, although these losses can
range as high as 2.5-3.0% in the South. Propionic acid, a biocide
used successfully to protect stored grains from microbiological
attack and from destructive self-heating, can be absorbed by wood
chips and effectively prevent the fungal degradation of the chips.
The cost for the quantity of acid required to protect chips during
outside storage is high.

Wood fiber insulating boards (8,11,12) have been know to undergo
spontaneous ignition, while in transit, due to insufficient cooling
after drying. This hazard can easily be eliminated by maintaining
sufficient moisture and by cooling the boards before stacking, rolling,
and shipping.

Paper rolls (2300-2800 lbs.)(7,11,61) are also subject to
spontaneous combustion while in transit. This can be due to several
factors (a) very dry rolls (0-3% moisture), (b) tight winding of
the rolls, (c) size, and (d) a high initial temperature. This hazard
can also be eliminated by increasing the moisture content to 5% or
greater.

The spontaneous combustion of coal (10-12,76-97), has been a
topic of interest and difficulty for the past two centuries. The
factors which are generally agreed to have the greatest effect on
the oxidation rates and ignition temperatures in coal are: (a)
particle size and pore structure -- the ignition temperature
generally decreases with decreasing particle size and oxidation
rates generally increase with decreasing particle size, (b) oxygen
concentration -- increasing oxygen concentration increases the oxidation
rate and decreases the ignition temperature of a particular coal
sample, and (c) amount of volatile matter -- as the volatile matter

increases, the ignition temperature decreases and the rate of oxidation
also tends to increase. Moisture also plays a pronounced role in
the oxidation of coal. The effect of moisture in favoring the oxi-
dation and self-heating of coal has been confirmed by various
researchers. It is evident from both practical and experimental
studies that coal-oxygen complexes are formed when freshly powdered
coal is exposed to air at ambient temperatures. These oxygenated
complexes are unstable and readily decompose to oxides of carbon
and water. The presence of adsorbed water has been proven to be a
necessary condition for the formation of these complexes, which
appears to be an essential step in the overall oxidation process
of coal. Preventive measures include (a) ventilation, (b) limited
mass, and (c) low temperature immersion carbonization -- immersing
the coal for short periods (5-15 minutes) in an inert liquid such as
silicone oil at temperatures between 350-400°C. This carbonization
technique effectively reduces the accessible pore volume of the
coal to levels at which heat generation through subsequent sorption
of moisture and oxygen is too slow to cause significant temperature
rises in a stockpile. It has also been established by infrared
spectroscopic scanning of the washed coal samples that little if
any oil penetrates into the coal during the immersion heating process (95).

Chemically activated carbon (11,79,88-94) is known to undergo
self-heating and ignition in transit and therefore must be adequately
cooled before it can be shipped and stored safely in bulk. Available
studies on charcoal and activated carbon show that the self-heating
is principally a consequence of the occlusion of oxygen. Moisture
contributes significantly to the initial stages of self-heating of
dry material at ordinary temperatures. The self-heating characteristic
of powdered activated carbons is also dependent on their manufacturing
process, e.g., steam activated or chemically activated. The use of
polyethylene liners or covers where practical, has proven successful
in the prevention of self-heating by restricting the flow of air
through these oxygen sensitive materials.

Lampblack (11,79) is subject to the same conditions only to a
greater degree. Ignition is fostered by its oily character. Lamp-
black from tar, tar oils, mineral oils, coal lignite, and peat
contains sulphur which on contact with iron can spontaneously ignite.
Storage and transport in large heaps should be avoided as far as
possible. Careful handling of this material can eliminate the danger
of spontaneous combustion.

Air-Hazardous Materials (Ref: 10,98-104,128,130,133, 140)

The exposure of a relatively large surface area of some metals
e.g., titanium, zirconium, iron, promotes its rapid reaction with
the oxygen of the air causing spontaneous combustion. It has been
suggested that there is a great probability that all metals become
pyrophoric when the ratio of surface-to-volume becomes sufficiently
high (98). By decreasing the particle size, the ratio of surface
to mass increases and the reaction (oxidation) on the surface
generates more heat per gram, resulting in a larger rise in temperature.

The degree of a material's pyrophoricity is critically dependent on
its particle size. Pyrophoric action results from the inability of
a material to dissipate its heat of oxidation (even slow oxidation)
in air rapidly enough, thus causing a rapid rise in temperature (100).
The large amounts of heat liberated during oxidation of a pyrophoric
powder can also cause explosion if the powder is suspended in air
as a dust. Pyrophoric action is not limited to powders of sub-
stantially pure metals but includes compounds as well as alloys.
This behavior occurs in the lower oxides of iron, manganese, and
uranium, the hydrides of uranium and cerium, and the carbides and
nitrides of uranium. It is generally true that the higher the heat
of formation of the metal oxide, the larger the particle size may
be and yet retain the ability to burn spontaneously. Almost any
alloy or compound will be pyrophoric if it is in fine enough
particles and if its heat of oxidation is strongly exothermic (100,
103). Examples of other pyrophoric materials include (a) metal
alkyls -- trimethyl aluminum, triethyl aluminum -- compounds
containing a very active organometallic bond capable of high
reactivity with oxygen, (b) metal carbonyls -- iron pentacarbonyl,
potassium carbonyl, and (c) metal hydrides -- aluminum hydride,
barium hydride, beryllium hydride. Pyrophoric substances can be
inactivated by opening the container under liquids such as
acetylcellulose in acetone, 96% ethyl alcohol, and in the case of
pyrophoric cobalt, even hydrocarbons. On evaporation of the
solvent, the pyrophor is protected against spontaneous ignition
by surface oxidation which occurs during the slow evaporation of
the solvent.

Water-Hazardous Materials (Ref: 103,111,121,127,130,140)

In general, active metals, hydrides, carbides, and phosphides
are incompatible with water because of the generation of flammable,
toxic, and/or explosive products. Cesium, potassium, sodium, and the
alloys of these metals can ignite spontaneously on exposure to air
and/or moisture. The degree of hazard depends to a great extent on
the probability of collecting a dangerous concentration of flammable
products. This depends on factors such as quantity of material
involved, ventilation, etc.

The following table (Table I) lists solid substances that are
subject to spontaneous ignition as well as materials that are
flammable due to reaction with air (air hazardous materials) and/or
moisture (water hazardous materials). The hazardous material
listing reported in Table I is compiled from data obtained from the
open literature, the Code of Federal Regulations (CFR-49) 1972, and
the Transport of Dangerous Goods (1970) - United Nations recommen-
dations, as well as unclassified government reports.

TABLE 1

Materials Subject to Spontaneous Combustion (105-130,137-141)

MATERIAL	REMARKS
Accelerene (para nitroso dimethyl aniline)	spontaneously flammable
Alfalfa Meal	subject to spontaneous ignition
Aluminum - Triethyl, Methyl, Palmitate, Diethylmonochloride	spontaneously flammable
Aluminum - Dust, Powder, Hydride	spontaneously flammable in air
Aluminum Phosphide	on reaction with water yields phosphine which is spontaneously flammable
Aluminum - Carbide, Ferrosilicon Powder	water hazardous material
Aluminum Silicon Powder	water hazardous material
Azido Thallium	explodes in air
Bags, Used - Burlap, Jute	tendency to ignition dependent on previous use
Barium	spontaneously flammable in moist air
Barium Azide	spontaneously flammable
Barium Carbide	spontaneously flammable on contact with water
Barium Hydride - Fine Powder	can spontaneously ignite in dry and moist air
Barium Perioxides	can react explosively with large quantities of water
Barium Sulfide	can ignite in dry and moist air
Beans - Locust, etc.	subject to spontaneous combustion
Benzyl Sodium	spontaneously flammable
Beryllium Powder	spontaneously flammable
Beryllium Dimethyl	spontaneously flammable in moist air
Bis-Cyclopentadienyl Manganese	spontaneously flammable in moist air
Bismuth	spontaneously flammable
Bismuth Ethyl Chloride	spontaneously flammable
Bismuth Pentafloride	reacts violently with water sometimes with ignition
Bone Meal, Bone Black, Bone Charcoal	subject to spontaneous combustion
Borohydrides of Al,Be,Zr,Hf	spontaneously flammable in air
Boron Dust	spontaneously flammable in air
Boron Chloride Tetramer	spontaneously flammable
Cacodyl Cyanide	spontaneously flammable
Cacodyl Phenyl	spontaneously flammable
Cadmium	spontaneously flammable
Cadmium Amide	can explode in water
Cadmium Nitride	spontaneously flammable in water

MATERIAL	REMARKS
Calcium Carbide	yields C_2H_2 on contact with water which can ignite
Calcium Hydride	dust can explode if dispersed in air
Calcium Hypochlorite	decomposes in water, vapors produced are flammable
Calcium Metal	finely divided material is spontaneously flammable in air
Calcium Nitride	spontaneously flammable in air
Calcium Oxide	violent reaction with water sometimes with ignition
Calcium Phosphide	reacts with water yielding phosphine which is spontaneously flammable
Calcium Silicide	spontaneously flammable
Calcium Silicon (Calcium Manganese Silicon)	spontaneously flammable
Calcium Sulfide	spontaneously flammable
Calcium Dithionate	spontaneously flammable
Celluloid, Scrap	subject to spontaneous ignition
Cerium	spontaneously flammable in air
Cerium III Aluminohydride	spontaneously flammable
Cerium Amalgam	spontaneously flammable in air
Cerium Hydride Amalgam	spontaneously flammable in air
Cerium Indium Alloy	spontaneously flammable, 0-30% Ce alloy has greatest pyrophoricity
Cerium Nitride	spontaneously flammable in moist air
Cesium Amide	possible explosion on contact with water
Cesium Antimony Alloy	spontaneously flammable
Cesium Arsenic Alloy	spontaneously flammable
Cesium Bismuth	spontaneously flammable
Cesium, Metal	spontaneously flammable in moist air at room temperature
Cesium Oxide	spontaneously flammable in water
Cesium Phosphide	spontaneously flammable in moist air and on contact with water
Cesium Silicide	ignites spontaneously on contact with water
Chromium	spontaneously flammable
Chromium Cobalt Alloy	spontaneously flammable when particle size is less than 1 micron
Chromous Monoxide	spontaneous
Coal - Bituminous, brown, fossil	subject to spontaneous ignition, tendency to self-heating depends on origin, nature and degree of volatile ingredients

TABLE 1 (Cont.)

MATERIAL	REMARKS
Cobalt	spontaneously flammable
Cobalt Amalgam	spontaneously flammable
Cobalt Nitride	spontaneously flammable
Cobalt Resinate	spontaneously flammable
Colophony Powder, Gum Rosin	subject to spontaneous combustion
Copper	fine powders are spontaneously flammable (.01-.03 microns)
Copper Aluminohydride	spontaneously flammable
Copper Pyrite or Copper Ore Concentrates	in large bulk - subject to spontaneous ignition
Copra	subject to spontaneous ignition
Cork	subject to spontaneous ignition
Cotton, Cotton Waste, Wet Cotton	subject to spontaneous ignition
Cupric Phosphide	spontaneously flammable in moist air and on contact with water
Decaborane	spontaneously flammable in air
Dibutyl Magnesium	spontaneously flammable
Diethyl Magnesium	spontaneously flammable
Diethyl Zinc	spontaneously flammable
Dimethyl Magnesium	spontaneously flammable
Diemthyl Zinc	spontaneously flammable
Dipotassium Nitroacetate	explodes when in contact with water
Disilyamino Dichloroborine	spontaneously flammable
Distillers Dried Grains	subject to spontaneous ignition, maintain moisture content between 7-10% and cool below 100°F before storage
Disulphur Dinitride	explodes in air above 30°C
Dust from blast furnace filters	subject to spontaneous ignition
Ethyl Lithium	spontaneously flammable
Ethyl Sodium	spontaneously flammable
Europium	oxidizes rapidly in air and may ignite spontaneously
Feeds, various	subject to spontaneous ignition
Ferrosilicon - containing >30% and <90% silicon	ignites on contact with water
Ferrous Oxide	spontaneously flammable in air
Fertilizers, Manure	subject to spontaneous ignition
Fibers - Bast, Cocoa, Coir, Esparto, Flax, Hemp, Jute, Oakum, Palmetto, Sisal, etc.	subject to spontaneous combustion, safe moisture content <6>20%
Films - if base is nitro-cellulose	subject to spontaneous ignition
Fish Meal, Fish Scraps	subject to spontaneous ignition, safe moisture content between 6-12%

TABLE 1 (Cont.)

MATERIAL	REMARKS
Grains, various	subject to spontaneous ignition
Hafnium	spontaneously flammable
Hay	subject to spontaneous ignition moisture control will eliminate this problem
Hexachlorethane Mixture	spontaneously flammable on contact with water
Hexamino Calcium	spontaneously flammable
Hides, various	subject to spontaneous combustion
Indium Monoxide	spontaneously flammable
Iron - filings, turnings, borings, powder, scrap, chips wool, etc.	subject to spontaneous ignition when present in large bulk, also when damp can under certain conditions liberate hydrogen which is flammable and explosive on mixture with air
Iron Amalgam	spontaneously flammable
Iron II Hydroxide	spontaneously flammable in air
Iron Pyrite, Iron Sulphide, Iron Disulphide	subject to spontaneous ignition in large bulk
Iron Oxide, spent or Iron Sponge, spent	subject to spontaneous ignition
Ixtle	subject to spontaneous combustion
Jaggery or Jaggery Sugar	subject to spontaneous combustion
Lamp Black	subject to spontaneous ignition
Lanthium Antimony Alloy	spontaneously flammable
Lead	pyrophoric powder produced from $Fe(OH)_3$ if reduction temperature is lower than 550°C
Lead Imide	explodes on contact with water
Lithium Aluminum Hydride	reacts with water and moist air forming hydrogen which is spontaneously flammable
Lithium Borohydride	spontaneously flammable on contact with moist air and water
Lithium Dimethylamide	spontaneously flammable
Lithium Hydride	spontaneously flammable
Lithium Hypochlorite	flammable on contact with water
Lithium Metal	spontaneously flammable on contact with moist air and water
Lithium Nitride	spontaneously flammable on contact with moist air and water

TABLE 1 (Cont.)

MATERIAL	REMARKS
Lithium Phosphide	spontaneously flammable in moist air and on contact with water
Lithium Silicide	spontaneously flammable
Lycopodium, Club Moss Seeds, Earth Moss Seeds, Vegetable Sulphur	can spontaneously ignite when scattered in air
Magnesium Aluminum Phosphide	spontaneously flammable on contact with water
Magnesium Cyanide	spontaneously flammable on exposure to air
Magnesium Diamide	spontaneously flammable on exposure to air
Magnesium Diphenyl	spontaneously flammable on contact with moist air and water
Magnesium Ethyl	spontaneously flammable in air
Magnesium Hydride	spontaneously flammable on contact with moist air and tap water
Magnesium, metal-powder, ribbon, chips	reacts with air and moisture evolving H_2 which ignites spontaneously
Magnesium Methyl	spontaneously flammable in air
Magnesium Phosphide	spontaneously flammable on contact with water
Manganese II Aluminohydride	spontaneously flammable
Manganese Bismuth Alloy	spontaneously flammable
Methyl Aluminum Sesquibromide	spontaneously flammable
Methyl Aluminum Sesquichloride	spontaneously flammable
Methyl Magnesium Chloride	spontaneously flammable
Methylene Dilithium	spontaneously flammable in air
Methylene Magnesium	spontaneously flammable
Methyl Lithium	spontaneously flammable
Methyl Sodium	spontaneously flammable
Molybdenum Metal	spontaneously flammable
Molybdenum Dioxide	spontaneously flammable
Molybdenum Trioxide	spontaneously flammable
Monomers - for polymerizations	subject to self-heating from spontaneous polymerization caused by heat and light
Nickel - Finely divided, activated or spent, wetted with not less than 40%, by weight, of water or other suitable liquid	spontaneously flammable (.01-.03 microns)
Nickel Carbonyl	in the presence of air forms a deposit which becomes peroxided which then tends to decompose and ignite
Nickel Iron Alloy	spontaneously flammable
Nickel Lanthium Alloy	spontaneously flammable

TABLE 1 (Cont.)

MATERIAL	REMARKS
Oils, animal and vegetable*	subject to spontaneous ignition
Oleic Acid	impregnated fibrous materials may self-heat unless ventilated
Paper, waste paper - treated with unsaturated oils, incompletely dried (includes carbon paper)	subject to spontaneous ignition
Pentaborane	spontaneously flammable
Phenyldiazosulfide	explodes when dried in air
Phenyl Magnesium Chloride	spontaneously flammable
Phenylsilver	explodes at room temperature
Phosphorus red-commercial	subject to spontaneous ignition in thick layers, critical thickness of layer defined by $Y=2X=[K(To-Ta)/Q]^{1/2}$ where Y = critical thickness of layer α in centimeters, above which spontaneous combustion occurs, X = distance in cm from plane of wax, K = heat transfer coefficient, To = autogenous temp., T_a = ambient temperature, Q = heat of reaction in cal/cc/sec. The thickness of the layer above which spontaneous ignition occurs is inversely proportional to the temp. of the rate of generation of heat which is directly proportional to the rate of oxidation of red phosphorus.
Phosphorus white or yellow	spontaneously flammable in air at 34°C, preserved under water
Phosphorus Pentasulfide	spontaneously flammable, can ignite on contact with moisture
Plastics	subject to spontaneous ignition
Plutonium	explosive reaction with water, ignites spontaneously in dry air
Plutonium Hydride	spontaneously flammable
p-Nitrosodimethylamiline	spontaneously flammable
Potassium	spontaneously flammable in air, also possibility of explosion
Potassium Antimony Alloy	spontaneously flammable
Potassium Arsenic Alloy	spontaneously flammable

*Some of the more common animal and vegetable oils in decreasing tendency to spontaneously ignite -- cod liver oil, fish oil, linseed oil, menhaden oil, perilla oil, > corn oil, cottonseed oil, olive oil, pine oil, red oil, soybean oil, tung oil, whale oil > castor oil, lard oil, black mustard oil, oleo oil, palm oil, peanut oil, -- avoid contact with any fibrous combustible materials.

TABLE 1 (Cont.)

MATERIAL	REMARKS
Potassium Borohydride	spontaneously flammable in water
Potassium Carbide	explosive reaction on contact with water
Potassium Carbonyl	detonates on contact with air and water
Potassium Chlorate	spontaneously explosive
Potassium Dithionite	spontaneously flammable
Potassium Graphite	spontaneously combustible in air
Potassium Hydride	spontaneously flammable in air
Potassium Metal Alloys	spontaneously flammable in water
Potassium Nitride	spontaneously flammable in air
Potassium Nitromethane	spontaneously flammable in water
Potassium Peroxide	spontaneously combustible and possibly explosive on contact with water
Potassium Phosphide	spontaneously flammable in moist air and on contact with water
Potassium Silicide	ignites explosively on contact with water
Potassium Sodium Alloys	water reactive material
Potassium Sulfide	may ignite spontaneously in air when anhydrous or containing < 30% water of crystallization
Prosiloxane	spontaneously flammable in air
Rags, used	spontaneously combustible tendency depends on previous use
Rubidium	ignites in air and on contact with water
Rubidium Antimony Alloy	spontaneously combustible
Rubidium Arsenic Alloy	spontaneously combustible
Rubidium Bismuth Alloy	spontaneously combustible
Rubidium Hydride	spontaneously flammable in moist air and water
Rubidium Phosphide	spontaneously flammable in moist air and water
Rubidium Silicide	spontaneously flammable in moist air and water
Samarium Carbide	evolves acetylene and hydrogen on contact with water
Samarium Dichloride	evolves acetylene and hydrogen on contact with water
Sawdust	subject to spontaneous combustion
Scrap Leather	subject to spontaneous combustion
Scrap Rubber	subject to spontaneous combustion
Seeds, seed cakes, seed expellers - containing vegetable oils	subject to spontaneous combustion
Silicides (of light metals)	decompose in water yielding hydrogen
Silicocyn	spontaneously flammable

TABLE 1 (Cont.)

MATERIAL	REMARKS
Silicon, dust	spontaneously flammable
Silicon Hydride	spontaneously flammable in air
Silicon Monoxide	spontaneously flammable
Siloxane	spontaneously flammable
Silver-fine powder	spontaneously flammable
Soap Powder	subject to spontaneous combustion when uninhibited
Sodium Acetate	possibility of spontaneous ignition when in contact with moist air or water
Sodium Aluminum Hydride	spontaneously flammable in water
Sodium Amalgam	spontaneously flammable on contact with moist air and water
Sodium Amide	ignites spontaneously on contact with water
Sodium Borohydride	ignites spontaneously on contact with water
Sodium Carbide	explosive reaction on contact with water
Sodium Carbonyl	detonates in air and water
Sodium Dithionate	may ignite on contact with water
Sodium Dithionite (Sodium Hydrosulphite)	may ignite on contact with water
Sodium Hydrazide	spontaneously flammable in moist air and water
Sodium Hydride	spontaneously flammable in moist air and water
Sodium Hydroxylamine	spontaneously flammable in air
Sodium Lead Alloy	spontaneously flammable in water and moist air
Sodium, Metal	decomposes in water forming hydrogen which ignites spontaneously
Sodium Nitromethane	spontaneously flammable in moist air
Sodium Phosphamide	spont neously flammable
Sodium Phosphide	reac with water and moist air
Sodium Potassium Alloy	spo neously flammable on reaction wi_i water
Sodium Silicide, powder	spontaneously flammable in moist air and possibly explosive on contact with water
Sodium Sulfide	spontaneously flammable in air
Stannic Chloride	reacts with water and evolves considerable heat
Stannic Phosphide	spontaneously flammable on contact with moist air and water
Stearic Acid	heats spontaneously
Straw of Flax, Maize, Oats, Rice, Rye, Wheat, etc.	subject to spontaneous heating and combustion

TABLE 1 (Cont.)

MATERIAL	REMARKS
Strontium Azide	spontaneously flammable
Strontium Metal	if finely divided ignites on exposure to air, also liberates hydrogen on contact with water
Strontium Phosphide	spontaneously combustible
Sulfur	possibility of spontaneous ignition
Sulfur Trioxide	violent reaction with water
Tankage	subject to spontaneous combustion
Textile Waste, wet	subject to spontaneous combustion
Tetrabromosilane	violent reaction with water
Thorium Hydride	spontaneously flammable
Thorium, metal	spontaneously flammable (high as powder, moderate as chips)
Thorium Nitride	spontaneously flammable in air
Thorium Oxysulfide	spontaneously flammable in air
Thorium Silver Alloy	spontaneously flammable
Tin	spontaneously flammable when finely divided
Titanium Bichloride	spontaneously flammable in air and water
Titanium Bromide	spontaneously flammable
Titanium Carbide, dust	spontaneously flammable in air
Titanium Chloride	spontaneously flammable in moist air
Titanium Dibromide	spontaneously flammable in moist air
Titanium Diiodide	ignites in moist air
Titanium Monoxide	spontaneously flammable
Titanium Trichloride	spontaneously flammable in air
Triazide Borine	spontaneously flammable in air and water
Trichlorosilane	reacts with water
Triisobutyl Aluminum	subject to spontaneous combustion
Triphenylaluminum	decomposes explosively in water
Tungsten,β	spontaneously flammable
Uranium Bismuth Alloy	spontaneously flammable, over 30% U very pyrophoric
Uranium Borohydride	spontaneously flammable and liable to detonate in air
Uranium Carbide	spontaneously flammable if particle size < 40 microns
Uranium Hydride	spontaneously flammable
Uranium Metal, powder	spontaneously flammable, if dry ignites in air, if dispersed it can explode in air
Uranium Monocarbide	spontaneously flammable, if < 40 microns - very pyrophoric
Uranium Nitride	spontaneously flammable
Uranium Oxide	spontaneously flammable

TABLE 1 (Cont.)

MATERIAL	REMARKS
Vanadium Sesquioxide	spontaneously flammable
Varnished Fabrics	subject to spontaneous combustion
Wood - chips, excelsior, sawdust shredded wood, wood flour, wood shavings, wood wool	subject to spontaneous combustion
Wool	subject to spontaneous combustion
Zinc Dithionite	spontaneously flammable
Zinc Metal, dust, ashes, powder filings, dross, chips, shavings, etc.	in the damp state may heat spontaneously and ignite on exposure to air
Zinc Phosphide	spontaneously flammable in moist air
Zirconium	spontaneously flammable in air
Zirconium Borohydride	spontaneously flammable
Zirconium Carbonitride	spontaneously flammable in air
Zirconium Dibromide	spontaneously flammable
Zirconium Metal, powder sponge, strips, coiled wire, sheets,etc.	spontaneously flammable in air

Other materials subject to spontaneous combustion include: dessiccated leather, leather scraps, dried blood, dried blood tankage, garbage tankage, leather meal, slaughter house tankage -- liable to spontaneously ignite which is dependent on (1) composition of the products, (2) method of drying, (3) degree of moisture, and (4) temperature at time of loading. The following materials are subject to spontaneous ignition especially when damp, greasy, oily or mixed with varnish - artifical wool, automobile brakeband lining, batting dross, canvas, feathers, felt, filter press cloth, hair, mungo, shoddy, twist, waterproofed cloth, waste wool, wool pickings, wool waste.

Conclusions (Ref: 1-21,43-49,111,131-136,138-145)

Substances subject to spontaneous combustion can be divided into the following categories:

(a) Substances which are noncombustible but can cause ignition as a result of spontaneous heating (calcium oxide, alkali, alkali earth oxides, etc.).

(b) Substances with low ignition temperature whose oxidation is allowed to proceed freely. The ratio of the surface exposed to the mass being heated is so great that heat is generated by oxidation more rapidly than it can be dissipated, and the temperature rises locally until the ignition point is reached. Pyrophoric character in general depends upon the nature and chemical reactivity of the material and varies with the amount of exposed surface and the physical condition of that surface (finely divided metals, hydrides of phosphorus, white phosphorus, etc.).

(c) Combustible substances which ignite spontaneously as a result of slow oxidation -- vegetable and animal fats and oils containing glycerides of unsaturated fatty oils that absorb oxygen into double bonds producing heat, coal, wood charcoal, wood products, etc.

(d) Materials where biological processes cause spontaneous ignition as a result of the metabolism of living organisms subsequently furthered by the absorption of oxygen - hay, grains, fish meal, sugar, peat, and other agricultural products.

(e) Materials which react with water, forming flammable or explosive products (active metals, hydrides, carbides, phosphides, etc).

Although the causes of spontaneous combustion are few, the conditions under which these factors may operate to create a dangerous situation are many and varied. In some cases more than one factor may be operative (oxidative and/or biological) and one may initiate conditions favorable to the functioning of another.

Except for air-hazardous (pyrophoric) and water-hazardous materials, the tendency of susceptible materials to heat is generally increased by elevated temperatures and by the insulating effect of the material alone or by surrounding conditions in transit or in storage. Spontaneous heating does progress in various materials without hazardous effects if the conditions are such that the generated heat is dissipated at a rate that prevents the material from reaching its critical temperature. This temperature varies for different materials but once reached, combustion can occur. Ventilation is thus an important factor in preventing many instances of potential spontaneous ignition, although a complete lack of ventilation is also a certain deterrent against combustion in cases

where fixed oxygen is not present in the material. This fact may be utilized where small quantities of material make practical the use of air tight containers or compartments.

Temperature measurements in the interior of a mass of material will give an indication of the progress of spontaneous heating. These temperatures, taken at various locations within the material would detect localized focal points where spontaneous heating could be occurring.

In the shipping and storage of agricultural products, the use of moisture control and biocides could reduce the hazard of spontaneous combustion and the self-heating of these materials.

REFERENCES

1. F. P. Rothbaum, Journal of Applied Chemistry, 13, 291, 1963.

2. H. P. Rothbaum, Ibid., 14, 165, 1964.

3. H. P. Rothbaum, Ibid., 7, 291, 1964.

4. R. E. Carlyle and A. G. Norman, Journal of Bacteriology, _, 669, 1941.

5. T. Gibson et al., Journal General Microbiology, 19, 122, 1958.

6. M. Milner et al., Cereal Chemistry, 24, 507, 1947.

7. C. F. Edwards and L. F. Rettger, Journal of Bacteriology, 34, 489, 1937.

8. J. B. Firth and R. E. Stuckey, Nature, 159, 624, 1947.

9. C. A. Broone, Science, 77. 223, 1933.

10. A. H. Nuckolls, Underwriters Laboratories Inc., Research Bulletin, 2,3, 1938.

11. W. W. Moore, National Fire Prevention Association Quarterly, 6,188, 1912.

12. N. D. Mitchell, Ibid., 45, 165, 1951.

13. A. K. Leont'ev and V. V. Pomerantsev translated for Zhur. Priklad. Khim., 33, 940, 1960.

14. N. N. Semenov, "Chemical Kinetics and Reactivity", Vol. 2, Pergamon Press. London, 1958.

15. D. A. Frank-Kamenetskii, "Diffusion and Heat Transfer in Chemical Kinetics," 2nd ed., Plenum Press, New York, 1969.

16. P. H. Thomas, Trans. Faraday Soc., 54, 60, 1958.

17. P. H. Thomas, "Ignition, Heat Release and Non-combustibility of Materials," ASTM STP 502, Phila. Pa., 56, 1972.

18. D. E. McDaniel, Ibid., 24, 1972.

19. I. K. Walker, W. J. Harrison and C. N. Hooker, N.Z.J. Sci., 8, 319, 1965.

20. I. K. Walker, W. J. Harrison and A. J. Read, Ibid., 10, 32, 1967.

21. I. K. Walker and A. J. Read, Ibid., 12, 302, 1969.

22. I. K. Walker, Ibid., 4, 309, 1961.

23. E. K. Rideal and A. J. B. Robertson, 3rd Symposium on Combustion, Flame and Explosion Phenomena, Williams & Wilkins Co., Balto., Md., P. 536, 1949.

24. J. L. C. Van Geel, Ind. Eng. Chem. (ind.) 58, 25, 1966.

25. N. J. Thompson, Ind. and Eng. Chem., 19, 394, 1927.

26. F. D. Snell and C. L. Hilton eds., Encyclopedia of Industrial Chemical Analysis, Interscience, New York.

27. ASTM D 2155-63T, Method of Test for Autoignition Temperature of Petroleum Products (Tentative), American Society for Testing and Materials, Philadelphia, Pa., 1965.

28. S. S. Penner and B. P. Mullins, "Explosions, Detonation, Flammability, and Ignition," Pergamon Press, London, 1959.

29. N. P. Setchkin, Journal of Research - NBS, Research Paper 2516, 53, 49, 1954.

30. P. C. Bowes, Journal of Applied Chemistry, 4, 140, 1954.

31. J. T. Geoghegan and E. H. Sheers, Rubber Age, 102, 63, 1970.

32. J. T. Geoghegan and E. H. Sheers, J. Chem. Educ., 45, A-429, 1968.

33. W. Helmore, "Science of Petroleum," Vol. 4, Oxford Press, p. 2970 1938.

34. J. M. Kutchta and A. F. Smith, Bureau of Mines Report of Investigation No. 7593, 1972.

35. Department of Transportation No. TSA-20-72-2, by C. M. Mason and V. C. Cooper, Bureau of Mines (Pittsburgh Mining and Safety Research Center Report No. 4160, 10 March 1972).

36. W. J. Scott, Advances in Food Research, 7, 83, 1957.

37. H. P. Rothbaum, Journal of Bacteriology, 81, 165. 1961.

38. I. K. Walker and W. J. Harrison, N.Z.J. agric. Res., 3, 861, 1960.

39. R. E. Du Four and C. C. Clogston, Underwriters Laboratories Research Bulletin No. 47, 5, 1953.

40. J. P. Foster, International Sugar Journal, 28, 603, 1926.

41. A. Schöne, Deut. Zuckerind, 36, 608, 1926.

42. M. I. Goldin, Bull. State Agr. Microbiol. (USSR), 8, 155, 1936.

43. M. K. Veldhuis, L. M. Christensen and E. I. Fulmer, Ind. Eng. Chem., _28_, 430, 1936.

44. R. O. E. Davis and J. O. Hardesty, Ind. Eng. Chem., _37_, 59, 1945.

45. J. O. Hardesty and R. O. E. Davis, Ibid., _38_, 1298, 1945.

46. Anon., Textil-Rendschau, _12_, 273, 1957.

47. I. K. Walker and H. M. Williamson, J. Appl. Chem. (London), _7_, 468, 1957.

48. I. K. Walker and W. J. Harrison, N.Z.J. Sci., _4_, 26, 1961.

49. I. K. Walker and W. J. Harrison, Ibid., _8_, 106, 1965.

50. W. D. Felix and H. Eyring, J. Text. Res., _33_, 465, 1963.

51. I. K. Walker, W. J. Harrison and G. F. Patterson, N.Z.J. Sci., _11_, 380, 1968.

52. A. J. Read, W. J. Harrison and I. K. Walker, Ibid., _10_, 964, 1967.

53. M. S. Carrie, I. K. Walker and W. J. Harrison, J. Appl. Chem., _9_, 608, 1959.

54. F. M. Fowkes et al., J. Agr. Food Chem., _8_, 203, 1960.

55. I. K. Walker and W. J. Harrison, N. Z. J. agric Res. _3_, 861, 1960.

56. M. Milner and W. F. Geddes, Cereal Chem., _23_, 449, 1946.

57. D. E. H. Frear, "Agricultural Chemistry," Vol. 2, D. van Nostrand Co., New York, 1951.

58. N. J. Thompson, Oil and Fat Industries, Nov., 317, 1928.

59. B. V. Ettling and M. F. Adams, Fire Technology, _7_, 225, 1972.

60. P. S. Hess and G. A. O'Hare, Ind. Eng. Chem., _42_, 1424, 1950.

61. M. B. Cunningham, Tappi, _44_, 194A, 1961.

62. F. L. Schmidt, Ibid., _52_, 1700, 1969.

63. E. L. Springer and G. J. Hajny, Ibid., _53_, 85, 1970.

64. G. H. Hajny, Ibid., _49_, 97A, 1966.

65. C. W. Rothrock Jr., et al., Ibid., _44_, 65, 1961.

66. J. K. Shields and H. H. Unligil, Pulp Paper Mag. Can., 69, 62, 1968.

67. G. H. Hajny et al., Tappi 50, 92, 1967.

68. E. Bjorkman and G. E. Haeger, Tappi, 46, 757, 1963.

69. J. C. McKee and J. W. Daniel, Ibid., 49, 47A, 1966.

70. W. C. Feist et al., Ibid., 56, 148, 1973.

71. R. M. Lindgren and W. E. Eslyn, Ibid., 44, 419, 1961.

72. T. P. Crane, Jr., and D. L. Fassnacht, Tappi, 43, 188A, 1960.

73. H. Greaves, Tappi, 54, 1128, 1971.

74. H. Greaves, Wood Sci. Technol., 5, 6, 1971.

75. W. E. Eslyn, Tappi, 56, 152, 1973.

76. S. La Vaun Merrill Jr., Fuel, 52, 61, 1973.

7   D. L. Carpenter and G. D. Sergeant, Fuel (London), 45, 429, 1966.

78. C. S. Finney and T. S. Spicer, Pyrodynamics, 1, 231, 1964.

79. D. W. Van Krevelen, "Coal", Elsevier Publ. Co., Amsterdam, 1961.

80. K. K. Bhattacharyya, Fuel, 51, 214, 1972.

81. K. K. Bhattacharyya, J. Mines Metals Fuels, 18, 5, 1970.

82. K. K. Bhattacharyya, Fuel (London), 50, 367, 1971.

83. R. L. Bond et al., Fuel (London), 29, 83, 1950.

84. R. E. Jones and D. T. A. Townend, 3rd Symposium on Kinetics and Mechanism of Combustion Reaction, p. 459, 1949.

85. M. Güney, Canadian Mining and Metallurgical Bulletin, 64, 138 1971.

86. W. Francis and R. V. Wheller, J. Chem. Soc., 2558, 1967.

87. M. Güney and D. J. Hodges, Chem. and Ind., 42, 1429, 1968.

88. A. Cameron and J. D. McDowall, J. Appl. Chem. Biotechnol., 22, 1007, 1972.

89. P. C. Bowes and A. Cameron, J. Appl. Chem. Biotechnol., 21, 244, 1971.

90. N. Boden et al., J. Appl. Chem. (London), 12, 145, 1962.

91. K. Akita, Rep. Fire Res. Inst. (Japan), 9, 1, 1959.

92. P. H. Thomas and P. C. Bowes, J. Appl. Physics (British), 12, 222, 1961.

93. T. Kinbara and A. Kawasaki, Bull. Fire Prevent. Soc., (Japan), 16, 9, 1967.

94. P. Gray and P. R. Lee, in Oxidation and Combustion Reviews, Vol. 2, Elsevier Publ. Co., London, 1967.

95. N. Berkowitz and J. G. Speight, Can. Min. Met. Bull., 66, 109, 1973.

96. G. E. Mapsone, Chem. and Ind. (London), 658, 1954.

97. N. Berkowitz and H. G. Schein, Fuel, 30, 94, 1951.

98. F. E. Littman and F. M. Church, AEC Research and Development Report - "A Study of the Spontaneous Ignition of Metals," SRI Project No. SU-2887, Contract No. AT(04-3)-115, Aug 15, 1960.

99. C. O. Nelson and D. B. Nelson, Sodium Air Reaction Experiments KAPL-639, Jan 1952.

100. B. Kopelman and V. B. Compton, Metal Progress, 63, 77, 1953.

101. E. J. Badin, 3rd Symposium on Combustion, Flame and Explosion Phenomena, Williams and Wilkins Co., Balto., Md., 1949.

102. J. E. Knapp et al., Ind. and Eng. Chem., 49, 874, 1957.

103. J. Marsel and L. Kramer, 7th Symposium (International) on Combustion, the Combustion Institute, Butterworth Scientific Publications, 1959.

104. W. R. Wilcox, Dangerous Materials - A Compatibility Study, General Electric Co., AD-766-947, St. Louis, MO, Feb 1973.

105. National Fire Prevention Association, National Fire Codes - Combustible Solids, Dusts and Explosives, Vol. 3, 492, 1964-65.

106. National Fire Prevention Association, Ibid., Vol. 3, 321, 1968-69.

107. J. R. Gibson and J. D. Weber, Handbook of Selected Properties of Air and Water Reactive Materials, U.S. Naval Ammunition Depot, Crane, IN RDTR No. 144, March 1969.

108. Bureau of Fire Prevention - City of Los Angeles, Dangerous Chemicals Code, Parker and Co., Los Angeles, CA, 1951.

109 J. Aeby, "Dangerous Goods and Others", Lloyd Anversois, Antwerp 4th ed., 1955.

110. A. Webster, Chem. and Ind. (London), 5, 502, 1958.

111. United Nations, "Transport of Dangerous Goods (1970), Vol. 1" ST/ECA/81/Rev. 2, E/CN.2/Conf. 5/10/Rev. 2, 1 Nov 1970.

112. European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR): Annex A - Provisions Concerning Dangerous Substances and Articles, Her Majesty's Stationery Office, London, 1970.

113. International Regulations Concerning the Carriage of Dangerous Goods by Rail (RID), Her Majesty's Stationery Office, London, 1973.

114. H. Zeiss, "Organometallic Chemistry," Reinhold Publ. Co., New York, 1960.

115. G. E. Coates, "Organo-Metallic Compounds," John Wiley and Sons Inc, New York, 1956.

116. D. T. Hurd, "An Introduction to the Chemistry of Hydrides," John Wiley and Sons Inc., New York, 1952.

117. H. C. Kaufman, "Handbook of Organometallic Compounds," D. Van Nostrand Co., Inc., New York 1961.

118. National Fire Prevention Association, National Fire Codes, Vol. 3, Boston, MA, 1965-66.

119. E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons Inc., New York, 1957.

120. N. I. Sax, "Dangerous Properties of Industrial Materials," Reinhold Publ. Corp., New York, 1963.

121. F. D. Snell and C. T. Snell, "Dictionary of Commercial Chemicals," D. Van Nostrand Co. Inc., New York, 1962.

122. R. A. Zingaro and R. E. McGlothlin, J. Chem. and Eng. Data, 8, 227, 1963.

123. J. R. Van Wazer, "Phosphorus and its Compounds," Vol. 1, Interscience Publ. Inc., New York, 1958.

124. W. Ripley, RDTN, No. 32, U.S. Naval Ammunition Depot, Crane, IN, Oct. 28, 1966.

125. National Fire Prevention Association, Fire Prevention Guide on Hazardous Materials, Boston, MA, 1966.

126. Metal Organic Compounds, Advances in Chemistry Series No. 23, American Chemical Soc., Wash. D. C., 1957.

127. P. G. Stechler et al., eds., "Merck Index of Chemicals and Drugs," Merck and Co., Rahway, New Jersey, 1960.

128. F. Paulden, Chemical Products, 10, 67, 1947.

129. F. Paulden, Chemical Products, 11, 26, 1948.

130. M. S. Silverstein et al., Ind. and Eng. Chem., 40, 301, 1948.

131. J. H. McGuire, Fire Technology, 5, 237, 1969.

132. H. H. Brown and N. J. Thompson, NFPA Quarterly, 25, 255, 1932.

133. C. A. Clifford, G. Hampel, and G. Hawley eds., Encyclopedia of Chemistry, Van Nostrand-Reinhold Co., 3rd ed., p. 291, 1973.

134. Thorpe's Dictionary of Applied Chemistry, 4th ed., Longman and Green and Co., New York, 1954.

135. V. Virtala, Valtion Teknillinene Tutkimuslaitoksen - Summary Translation, Julkaisuja, Helsinki, 14, 57, 1949.

136. A. S. Minton, Trans. Inst. Marine Engrs, 75, Suppl. i, 1963.

137. W. H. Shearon Jr., Chem. and Eng News, 29, 17, 1951.

138. Guide to Precautionary Labeling of Hazardous Chemicals, Manufacturing Chemists Assoc., inc., 6th ed., Wash. D.C., 1961.

139. H. Fawcett and W. S. Wood, "Safety and Accident Prevention in Chemical Operation," Interscience, New York, 1965.

140. J. F. Nobis, Ind. and Eng. Chem., 49, 44A, 1957.

141. A. K. Leont'ev in Oxidation and Combustion Reviews, Vol. 2, Elsevier Publ. Co., London, 1967.

142. J. T. Garrett, Safety Maintenance and Production, 112, 26, 1956.

143. R. D. Minteer, Ind. Eng. Chem., 47, 1202, 1955.

144. J. B. Firth, Proc. 3rd Conf. Chem. Wks. Safety, 89, 1950.

145. C. C. Concannon, Chem. Eng. News, 29, 3612, 1951.

DISTRIBUTION

Copies

Department of Transportation   6
Office of Assistant Secretary for
  Environment, Safety and Consumer Affairs
Office of Hazardous Materials
Washington, DC 20590
  Attn: Mr. Erskine E. Harton, Jr.

Defense Documentation Center   12
Cameron Station
Alexandria, VA 22314

TO AID IN UPDATING THE DISTRIBUTION LIST
FOR NAVAL SURFACE WEAPONS CENTER, WHITE
OAK LABORATORY TECHNICAL REPORTS PLEASE
COMPLETE THE FORM BELOW:

TO ALL HOLDERS OF __NSWC/WOL/TR 75-159__
by Eleonore G. Kayser, Code WR-11
DO NOT RETURN THIS FORM IF ALL INFORMATION IS CURRENT

A. FACILITY NAME AND ADDRESS (OLD) (Show Zip Code)

NEW ADDRESS (Show Zip Code)

B. ATTENTION LINE ADDRESSES:

C.

☐ REMOVE THIS FACILITY FROM THE DISTRIBUTION LIST FOR TECHNICAL REPORTS ON THIS SUBJECT.

D.
NUMBER OF COPIES DESIRED _____